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Synthesis of Ta_2O_5 Nanotubes for Photogeneration of H_2

Maurício O. Vaz[1], Marco V. Becker[1], Iasmim Biasi[1], Melissa M. Rodrigues[1,2], Tiago C. Severo[3,4,*], Célia de F. Malfatti[2], Sérgio R. Teixeira[1]

[1]Instituto de Física, Universidade Federal do Rio Grande do Sul, (UFRGS), Brazil
[2]Departamento de Metalurgia, Escola de Engenharia, Universidade Federal do Rio Grande do Sul (UFRGS), Brazil
[3]Programa de Pós-Graduação em Microeletrônica (PGMICRO), Universidade Federal do Rio Grande do Sul (UFRGS), Brazil
[4]Centro de Ciências Exatas da Natureza e de Tecnologia, Universidade de Caxias do Sul (UCS-CARVI), Brazil

Abstract The aim of this work was the optimization of nanotube synthesis parameters maximizing the H_2 photoproduction by *water splitting*. To reach this maximization, the anodization of Ta (Tantalum) was investigated by variation of electrical parameters during process. In this work variations of 1, 5, 10, 25 and 50V/s were applied during 20 minutes / each sample. After the anodizing process, vertical nanotubes were grown with well-defined morphology and aligned with the substrate. All samples were crystallized at 800 °C for 1 hour and an orthorhombic form was visualized by Scanning Electron Microscopy. The photocatalytic activity of Ta_2O_5 nanotubes was evaluated from the photolysis of water, using a quartz reactor and a solar simulator 240W-Xe/Hg lamp. The H_2 production was quantified by Gas Chromatography. Focused at the hydrogen production, it was observed that the best sample was obtained with a rate of increase of 1V/s.

Keywords Ta_2O_5, Nanotubes, Water Splitting; H_2 Production

1. Introduction

Presently, the investigation of clean and renewable sources of energy to replace fossil fuel is a significant research field in nanotechnology. [1] In this context, the research of hydrogen (H_2), as a fuel, gained significance, because it can generate electricity without emission of polluting gases into atmosphere. A possible reaction for H_2 generation is the dissociation of water (H_2O) into hydrogen (H_2) and oxygen (O_2) in the presence of sunlight and a semiconductor metal oxide photocatalyst. This process is known as *water splitting* [2] and occurs by adjustments of the photocatalyst energy bands to visible light.

In this process, the reactions of oxidation (forming O_2) and reduction of water (forming H_2) occurring on the surface of the photocatalyst, which exhibits the functions of anode and cathode. This is due to the fact that the catalyst is a metal oxide semiconductor, which gives a structure of driving band (BC) separated from the valence band (VB) by a known energy interval per band gap, characteristic for each compound. [3-5]

For the reaction to occur, the energy bands must be in proper positions, BC with less potential than the reduction potential of the H^+/H_2 (0.0EV) and BV with higher potential than the oxidation potential of H_2O /O_2 (1,23eV). Thus, the band gap of the semiconductor metal oxide used should be at least 1.23 eV. [3-5]

For this reason, the Tantalum Pentoxide (Ta_2O_5) is a promising compound, because it has a band gap of about 4.0 eV, proper positioning of the band energies and excellent chemical stability in aqueous solutions. [3-5]

The reaction in the photocatalyst surface is as follows: the valence band electrons are excited by the energy radiated to the conduction band, generating gaps in the valence band.

The pairs of electron-hole, when not undergoing recombination, migrate toward the semiconductor surface that respectively reduce and oxidize water molecules.

During the reaction, it is used a sacrificial agent, such as ethanol, to increase the efficiency of photocatalytic reaction. For our reactions, we used ethanol as a sacrificial agent, which acts by donating electrons to the valence band and not allowing the recombination of the electrons of the conduction band.

In recent years, the study of these photocatalysts has reduced the size of their structures for nanoscale and it was able to improve performance with greater efficiency. [3-5]

The production of photocatalyst is made by means of an anodic reaction. The anodizing process is an electrochemical able to create a protective oxide layer on the surface of a metal. During this process two simultaneous reactions occur, the oxidation of the anode and the reduction of the cathode.

The electric potential creates an intense electric field between the electrodes and causes the oxygen ions present in the electrolyte migrate to the surface of the anode, leading to growth of tantalum pentoxide. The formation of nanotubes is due to the use of hydrofluoric acid, as F-ions in solution to promote dissolution of the metal oxide, forming nanopores

* Corresponding author:
tcsevero@ucs.br (Tiago C. Severo)
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that deepens due to the generated electric field and grow increasingly resulting in the nanotubes. [3-5]

The aim of this study was to optimize the nanotube synthesis parameters and to maximize the photoproduction of H_2.

2. Methodology

For the anodizing, it was used an electrolyte solution consisting 95% by volume sulfuric acid (H_2SO_4), 1% hydrofluoric acid (HF) and 4% of distilled water, in a plastic beaker immersed in an ultrasound thermal bath at the temperature of 40 °C.

Within the solution are submerged two electrodes, one containing metallic tantalum (anode) and other containing metallic copper (cathode), subjected to electric potential. In addition, a voltage source, voltage source controller, computer and software for controlling the applied voltage ramp and for storing the data of electrical current obtained during the process.

The nanotubes of Ta_2O_5 were formed under different voltage increase rates (1, 5, 10, 25 e 50 V/s) for 20 minutes, analyzed by Scanning Electron Microscopy (SEM). The grain size was evaluated by X-ray diffraction using the Scherrer equation.

The photocatalytic activity of Ta_2O_5 nanotubes was evaluated by hydrogen photogeneration from the photolysis of water, in a double walled quartz reactor with room temperature water circulation (25 °C) to avoid overheating. The reactor was exposed to a solar simulator that contained a lamp of Xe/Hg of 240W. The gaseous products of the photocatalytic reaction were quantified by gas chromatography using argon as carrier gas. The generated gas was analyzed at 30-minute intervals through sample collections using a syringe of gas with valve. The reaction of hydrogen photogeneration was analyzed by 150 min.

3. Discussion of Results

The strategy used in this study was to investigate the influence of increased tension rate regarding the morphology of the Ta_2O_5 nanotubes; consequently, to check the influence of morphology in the production of H_2.

3.1. Effect of Rate of Increase Tension on Ta_2O_5 NTs Formation

In this study, it was found that the variation of the strain rate did not influence the formation of NTs of Ta_2O_5. In Figure 1, you can see the morphology of Ta_2O_5 NTs formed, rated by scanning electron microscopy (SEM).

According to the SEM images (Figure 1), the anodizing metallic Ta for 20 min resulted in the formation of a morphology nanotubular (NTs) vertically aligned, independent of the voltage rate used. Also, it was found that the orthorhombic crystal structure was obtained in all NTs after heating treatment at 800 °C for 1 hour, as evidenced by Figure 2. According to the literature [6, 7], the same orthorhombic crystal structure for Ta_2O_5 was found, in other nanostructures formed of tantalum oxide, for example, nanoparticles, there is a similar crystalline configuration. [6, 8]

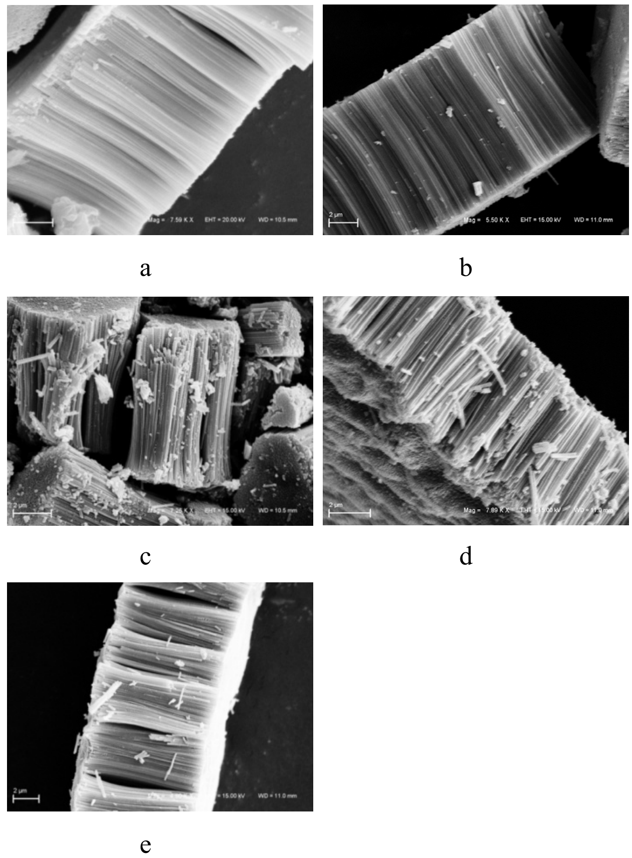

Figure 1. SEM image of the NTs formed with strain rate: a) 1 v/s; b) 5 v/s; c) 10 V/s; d) 25 v/s e e) 50 v/s at time 20 min

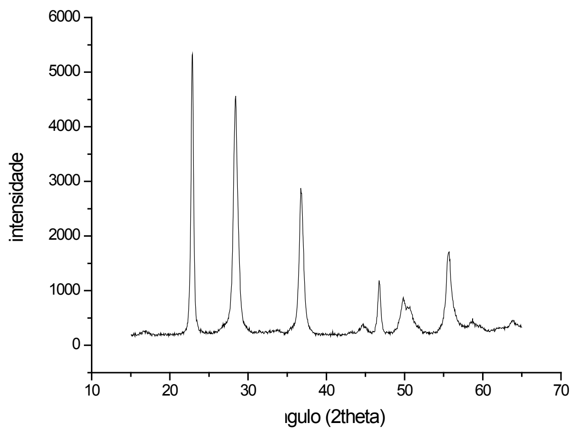

Figure 2. Diffractogram with features JSPD (25-0922). [6]

3.2. Hydrogen Production

The photocatalytic activities of the NTs of Ta_2O_5 obtained by anodizing process, under different strain rates increase, were evaluated by water photolysis process. Table 1 shows the results of obtained hydrogen production of different NTs of Ta_2O_5 formation.

The results shown in Table 1 showed decreasing production of H_2 as a function of increasing strain rate.

Table 1. Influence of voltage rise rate in the production of H_2

Sample	Characteristics of the Sample	Hydrogen production in mol/h.g
a	50V-1V/s-40°C-20'-800°-1H	1,70E-03
b	50V-5V/s-40°C-20'-800°-1H	9,68E-04
c	50V-10V/s-40°C-20'-800°-1H	1,43E-03
d	50V-25V/s-40°C-20'-800°-1H	1,05E-03
e	50V-50V/s-40°C-20'-800°-1H	8,61E-04

For better discussion of the results, the grain size was evaluated by X-ray diffraction using the Scherrer Equation. The results showed that increasing the strain rate used in the formation of NTs of Ta_2O_5 contribute to the increase of grain size. The sample with the lowest grain size was that presented in the higher rates of H_2 production. The smaller the crystallite size, smaller the migration path of the electronic load to the semiconductor surface.

4. Conclusions

According to the results presented, it was observed that the anodizing of Ta metal resulted in the formation of nanotubes vertically aligned, independent of the voltage rise rate used. Also, it was found that the crystal structure obtained in all NTs was orthorhombic after heating treatment at 800 °C for 1 hour. The photocatalytic activity of the NTs of Ta_2O_5 obtained by anodizing process, under different rates strain increase, was evaluated by water photolysis process and the H_2 production in all tested samples was observed.

REFERENCES

[1] K. Le, D. Martin, J. Tang, *Chinese Journal of Catalysis*, 32, 879-890, 2011

[2] A. Fujishima, K. Honda, *Nature*, 238, 37, 1972

[3] H. Wender, L. F. de Oliveira, A. F. Feil, E. Lissner, P. Migowski, M. R. Meneghetti, S. R. Teixeira, J. Dupont, *Chem Commun,* 46, 7019-7021, 2010.

[4] T. Kasuga, M. Riramatsu, A. Hoson, T. Sequino, K. Niihara, *Langmuir*, 14, 3160-3163, 1998.

[5] Y. Fan, D. Li, M. Deng, Y. Luo, Q. Meng, *Frontiers of Chemistry in China*, 4, 343-351, 2009.

[6] R. Gonçalves, P. Migowski, H. Wender, D. Eberhardt, D. E. Weibel, C. Sonaglio, M. J. M. Zapata, J. Dupont, A. F. Feil, and S. R. Teixeira, "Ta 2 O 5 Nanotubes Obtained by Anodization: E ff ect of Thermal Treatment on the Photocatalytic Activity for Hydrogen Production," 2012.

[7] R. V Goncalves, R. Wojcieszak, P. M. Uberman, S. R. Teixeira, and L. M. Rossi, "Insights into the active surface species formed on Ta2O5 nanotubes in the catalytic oxidation of CO," *Phys Chem Chem Phys*, vol. 16, no. 12, pp. 5755–5762, 2014.

[8] J. Liu, J. Liu, and Z. Li, "Preparation and photocatalytic activity for water splitting of Pt–$Na_2Ta_2O_6$ nanotube arrays," *J. Solid State Chem.*, vol. 198, pp. 192–196, Feb. 2013.